



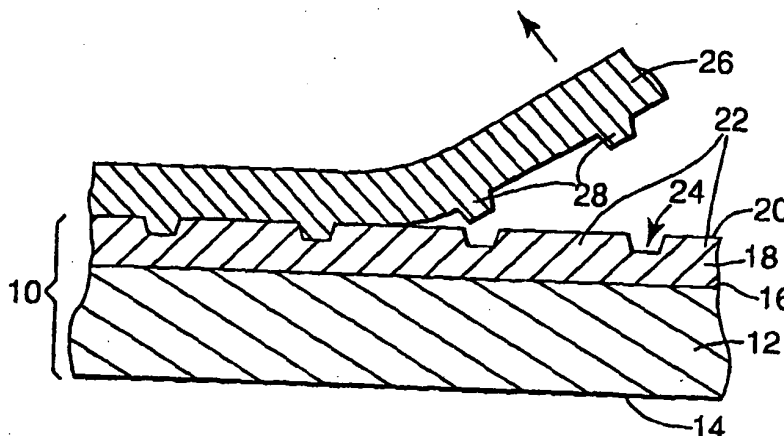
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : <b>C09J 7/02</b>	<b>A1</b>	(11) International Publication Number: <b>WO 00/69985</b> (43) International Publication Date: 23 November 2000 (23.11.00)
(21) International Application Number: PCT/US99/23020 (22) International Filing Date: 1 October 1999 (01.10.99) (30) Priority Data: 09/311,101                      13 May 1999 (13.05.99)                      US (71) Applicant: 3M INNOVATIVE PROPERTIES COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventors: MIKAMI, Haruyuki; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). FLEMING, Patrick, R.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). MAZUREK, Mieczyslaw, H.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: SZYMANSKI, Brian, E. et al.; 3M Innovative Properties Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  Published With international search report.	

(54) Title: ADHESIVE-BACKED ARTICLES

## (57) Abstract

An adhesive-backed article having a compliant film with a pressure sensitive adhesive bonded to one surface of the film. The pressure sensitive adhesive includes a microstructured surface opposite the compliant film. The microstructured surface defines channels in the adhesive. The channels create pathways for the egress of fluids. Upon application onto a substrate, the channels and structures wet out to render the microstructured surface substantially undetectable when viewed from the exposed surface of the article.



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

## ADHESIVE-BACKED ARTICLES

### Field of the Invention

The present invention relates to an adhesive-backed article, more particularly to  
5 such an adhesive-backed article having an adhesive with a microstructured surface  
bonded to a compliant film, and even more particularly to channels, with a specific  
volume per unit area, formed by the microstructured surface in the adhesive which  
permit the desirable properties of positionability and fluid egress to a periphery of the  
article without adversely affecting the surface appearance of the film after application  
10 onto a substrate.

### Background of the Invention

Films are often bonded to substrates utilizing pressure-sensitive adhesives.  
The films are generally bonded to a variety of different substrates including, for  
15 example, surfaces on motor vehicles. The interface between the adhesive and the  
contact surface of the substrate is important to the performance of the film. The  
interface between the adhesive and the substrate is affected by several factors. For  
example, the application may be affected by the type of adhesive used, the size and  
type of the films utilized, the surface of the substrate upon which the article is  
20 applied, the application technique utilized, or combinations thereof.

Adhesive-backed films are often used for decorative purposes. The  
placement of a film into a specific position prior to the formation of a bond between  
the adhesive and the substrate is often difficult, but important for aesthetic reasons.  
Some adhesive-backed articles are unable to slide on the surface of the substrate  
25 and will adhere with the slightest contact on the surface of the substrate. Such  
articles can often be particularly difficult to reapply if they inadvertently adhere to  
the substrate. The inability to slide the adhesive-backed article in place can  
adversely affect the positioning of the article or cause damage to the article upon  
attempted repositioning after adhesion.

30 The decorative articles also require that the adhesive-backed article be able  
to evacuate air or other fluids trapped underneath the adhesive during the bonding

step. The ability to bleed fluids and eliminate bubbles from underneath the article improves the overall appearance of the article. Additionally, bubbles under a film can adversely affect the adhesive performance of the article.

Thin films are often utilized on surfaces so that the adhesive film blends with the substrate upon which the film is applied. Additionally, thinner films are generally more flexible and therefore suited for application on contoured surfaces. However, the utilization of thin films can create an appearance problem. The thinner films have a tendency to show all surface abnormalities or uneven portions of either the adhesive or the substrate upon which the adhesive-backed article is applied.

#### Summary of the Invention

The present invention relates to an adhesive-backed article. The article includes a compliant film with a pressure sensitive adhesive bonded to a lower surface of the film. The pressure sensitive adhesive includes a microstructured surface opposite the compliant film.

In accordance with the present invention, the microstructured surface defines channels in the pressure sensitive adhesive. The channels comprise a volume of at least  $1 \times 10^3 \mu\text{m}^3$  per any 500  $\mu\text{m}$  diameter circular area in the adhesive. The channels are utilized to create exit pathways for fluid egress to a periphery of the article when the article is applied to a substrate. The adhesive-backed article sufficiently bonds to a substrate as indicated by a wet out value of at least 85%. The channels are substantially undetectable on an upper surface after final application of the article onto a substrate.

In general, the adhesive-backed article of the present invention is positionable over a substrate prior to forceful application of the article onto the substrate. The microstructured surface of the adhesive permits the article to either slide over the surface of a substrate, or be easily removed from the surface of the substrate, until enough pressure is applied to enable a bond between the adhesive and the surface of the substrate. The article of the present invention also enhances the egress of fluid from the interface between the adhesive and the substrate as a

bonding force is applied to the article. The microstructured features are particularly suited for applications utilizing thin films, ie less than 300  $\mu\text{m}$ .

The channels of the present invention can take various shapes or patterns. The channels are generally formed by structures in the adhesive that create the  
5 microstructured surface. The structures may be either placed randomly about the surface of the adhesive or placed in regular patterns.

The microstructured surface can be formed by directly embossing the pressure sensitive adhesive layer with the structures. Alternatively, a liner or backing can be embossed first and then coated with a pressure sensitive adhesive to  
10 impart the structures to the adhesive. The film is typically laminated or bonded to a side of the adhesive layer opposite the microstructured features.

It is an advantage to provide an adhesive-backed article that has pathways in the adhesive for fluid egress and permits positioning of the article without adversely affecting the appearance of the article. The channels define pathways to the  
15 periphery of the article that permit the flow of fluid trapped between the adhesive and the surface of the substrate. Additionally, the microstructured surface of the present invention enable the positioning of the article onto a substrate. Further, the microstructured adhesive does not result in observable periodic patterns on the exposed surface of the film after application of the article onto a substrate.

20 For purposes of the present invention, the following terms used in this application are defined as follows:

"microscopic" refers to structures of small enough dimension so as to require an optic aid to the naked eye when viewed from any plane of view to determine its shape. One criterion is found in Modern Optic Engineering by W. J. Smith, McGraw-Hill, 1966, pages 104-105 whereby visual acuity, "... is defined and  
25 measured in terms of the angular size of the smallest character that can be recognized." Normal visual acuity is considered to be when the smallest recognizable letter subtends an angular height of 5 minutes of arc on the retina. At typical working distance of 250 mm (10 inches), this yields a lateral dimension of  
30 0.36 mm (0.0145 inch) for this object;

"microstructure" means the configuration of structures wherein at least 2 dimensions of the structures are microscopic. The topical and/or cross-sectional view of the structures must be microscopic.;

5 "embossable" refers to the ability of a pressure-sensitive adhesive layer or liner to have part of its surface raised in relief, especially by mechanical means;

"wetting" or "wet out" means spreading out over and intimately contacting a surface;

10 "positionable" or "positionability" refers to those adhesive-backed articles that can easily slide over a substrate without grabbing or bonding to the substrate absent the application of a force, or adhesive-backed articles that upon light force are capable of releasably bonding to a substrate and upon removal retain at least some form of the original microstructured surface;

15 "release liner", used interchangeably with the term "liner", refers to a flexible sheet which after being placed in intimate contact with pressure-sensitive adhesive surface may be subsequently removed without damaging the adhesive coating;

"microstructured liner" refers to a liner with at least one microstructured surface, which is suitable for contact with an adhesive;

20 "backing" refers to a thin, flexible sheet which, after being placed in intimate contact with pressure-sensitive adhesive can not be subsequently removed without damaging the adhesive coating;

"microstructured backing" refers to a backing with a microstructured surface.

"substrate" refers to a surface to which the pressure-sensitive adhesive coating is applied for an intended purpose;

25 "tape" refers to a pressure-sensitive adhesive coating applied to a backing.

"inelastic deformation" means the permanent set at a given strain resulting from a film being stretched to 15% under tension and dissipating that tension.

30 "compliant" refers to a polymeric film that is soft and flexible as well as having sufficient inelastic deformation after being stretched so that once stretched, the film does not recover to its original length;

“bleedability” or “air-bleedability” refers to the egress of fluids, particularly air, from the interface between the adhesive and the surface of the substrate; and

“appearance” means the visual characteristics of the article as viewed from the exposed surface of the film after application of the article onto a substrate.

5

#### Brief Description of the Drawings

The invention will be more fully appreciated with reference to the following drawings in which similar reference numerals designate like or analogous components throughout and in which:

10        FIG. 1 is an enlarged, fragmentary, cross-sectional view of an adhesive-backed article according to the invention;

          FIG 2a is a segmented planar view of a microstructured adhesive surface according to the present invention;

15        FIG. 2b is a segmented view of the adhesive backed article highlighting the microstructured features of the present invention;

          FIG. 3a is a perspective view of one embodiment of a microstructured feature according to the present invention;

          FIG 3b is a perspective view of one embodiment of a truncated microstructured feature according to the present invention;

20        FIG 4a is a perspective view of one embodiment showing a double featured microstructured element according to the present invention;

          FIG 4b is a perspective view of another embodiment showing a double featured microstructured element according to the present invention;

25        FIG. 5 is a sectional view showing the configuration of a microstructured surface of an adhesive layer;

          FIG. 6 is a sectional view showing a second configuration of microstructured surface of an adhesive layer;

          FIG. 7 is a sectional view showing an additional configuration of a microstructured surface of an adhesive layer;

30        FIG. 8 is a perspective view of a release liner suitable for forming a microstructured surface in an adhesive according to the present invention;

FIG. 9 is a graph indicating the surface roughness of the article of the present invention after it is applied onto a substrate; and

FIG. 10 is a graph indicating the surface roughness of a comparative article after it is applied onto a substrate.

5

#### Detailed Description

The present inventive article 10, as depicted in FIG. 1, includes a compliant film 12 having an opposing surfaces 14, 16. A pressure sensitive adhesive 18 is bonded to surface 16 of the compliant film 12. The pressure sensitive adhesive 18 includes a surface 20 that can be bonded to a substrate (not shown). The pressure sensitive adhesive 18 includes structures 22 which define channels 24. A release liner 26 is releasably attached to the pressure sensitive adhesive 18. The release liner 26 includes protrusions 28 that are utilized to form corresponding channels 24 and structures 22 in the pressure sensitive adhesive 18. The release liner 26, shown in a partially removed state, is fully detachable and is used to protect the pressure sensitive adhesive prior to application of the article 10 on a substrate.

The article of the present invention is an improvement over structured adhesives that provide some degree of egress for entrapped air. However, certain structured adhesives are not easily positioned on a substrate. Further, the structures often show through the outer surface of the film after forceful application of the article onto the substrate. This is particularly true with thin films that tend to highlight any underlying surface differences. The present invention imparts a microstructured surface which defines channels in a pressure sensitive adhesive with specific rheological characteristics to address the issues associated with conventional adhesive-backed articles. The channels in the adhesive of the present invention have specific dimensions and characteristics to improve the positionability and fluid egress to a periphery of the article. Additionally, the characteristics of the channels render the microstructured surface of the adhesive substantially undetectable to the human eye when viewed from the exposed surface of the article after application.



The compliant film utilized in the present inventive article is generally made of various plastic materials used conventionally by those skilled in the art. Suitable films include, for example, vinyl, polyvinyl chloride, plasticized polyvinyl chloride, polyurethane, polyethylene, polypropylene, fluororesin or the like. The thickness of the film can vary widely according to a desired application, but is usually within a range from about 300  $\mu\text{m}$  or less, and preferably about 25  $\mu\text{m}$  to about 100  $\mu\text{m}$ .

A specific example of a suitable compliant layer is a plasticized polyvinyl chloride film, and has sufficient inelastic deformation after being stretched so that when stretched, the film does not recover to its original length. Preferably, the film has an inelastic deformation of at least 5% after being stretched once to 115% of their original length. A typical formulation of the vinyl film includes polyvinyl chloride resin, light and/or heat stabilizer(s), plasticizer, and optionally, pigment. The amount of plasticizer is generally less than about 40% by weight, and is preferably composed of polymeric non-migratable plasticizers which are compatible with the vinyl film and provide the necessary flexibility and durability. A suitable plasticizer is a combination of polymeric polyester elastomer and an ethylene vinyl acetate copolymer (such as Elvaloy 742 made by DuPont Co.) soluble in aromatic solvents and present in amounts of about 26 parts and 10 parts, respectively, per 100 parts vinyl resin.

Primers may optionally be used to enhance the bond between the film and the adhesive. The type of primer will vary with the type of film and adhesive used and one skilled in the art can select an appropriate primer. Examples of suitable primers include chlorinated polyolefins, polyamides, and modified polymers disclosed in U.S. Patent Nos. 5,677,376, 5,623,010 and those disclosed in WO 98/15601 and WO 99/03907, and other modified acrylic polymers. Typically, primers are dispersed into an adequate solvent in very low concentrations, e.g., less than about 5% solids, and coated onto the film, and dried at room or elevated temperatures to form a very thin layer. Typical solvents used may include water, heptane, toluene, acetone, ethyl acetate, isopropanol, and the like, used alone or as blends thereof.

In accordance with the present invention, useful pressure sensitive adhesives include those which are capable of retaining microstructured features on an exposed surface after being embossed with a microstructured molding tool, backing or liner, or after being coated on a microstructured molding tool, backing or liner from which it is subsequently removed. The particular pressure sensitive adhesive selected for a given application is dependent upon the type of substrate the article will be applied onto and the microstructuring method employed in producing the adhesive-backed article. Additionally, useful microstructured pressure sensitive adhesives should be capable of retaining their microstructured surfaces for a time sufficient to allow utilization of the adhesive-backed article.

Any pressure-sensitive adhesive is suitable for the invention. Adhesives are typically selected based upon the type of substrate that they are to be adhered to. Classes of pressure-sensitive adhesives include acrylics, tackified rubber, tackified synthetic rubber, ethylene vinyl acetate, silicone, and the like. Suitable acrylic adhesives are disclosed, for example, in U.S. Patent Nos. 3,239,478, 3,935,338, 5,169,727, RE 24,906, 4,952,650, and 4,181,752. A preferred class of pressure-sensitive adhesives are the reaction product of at least alkyl acrylate with at least one reinforcing comonomer. Suitable alkyl acrylates are those having a homopolymer glass transition temperature below about  $-10^{\circ}\text{C}$  and include, for example, n-butyl acrylate, 2-ethylhexylacrylate, isooctylacrylate, isononyl acrylate, octadecyl acrylate and the like. Suitable reinforcing monomers are those having a homopolymer glass transition temperature about  $-10^{\circ}\text{C}$ , and include for example, acrylic acid, itaconic acid, isobornyl acrylate, N,N-dimethylacrylamide, N-vinyl caprolactam, N-vinyl pyrrolidone, and the like.

The adhesives may be polymers that are dispersed in solvent or water and coated onto the release liner and dried, and optionally crosslinked. If a solventborne or waterborne pressure-sensitive adhesive composition is employed, then the adhesive layer must undergo a drying step to remove all or a majority of the carrier liquid. Additional coating steps may be necessary to achieve a smooth surface. The adhesives may also be hot melt coated onto the liner or microstructured backing. Additionally, monomeric pre-adhesive compositions can

be coated onto the liner and polymerized with an energy source such as heat, UV radiation, e-beam radiation.

The thickness of the adhesive is dependent upon several factors, including for example, the adhesive composition, the type of structures used to form the microstructured surface, the type of substrate, and the thickness of the film. Those skilled in the art are capable of adjusting the thickness to address specific application factors. In general, the thickness of the adhesive layer is greater than the height of the structures which comprise the microstructured surface. Preferably, the thickness of the adhesive layer is within a range from about 10 to about 50  $\mu\text{m}$ .

The pressure sensitive adhesive can optionally include one or more additives. Depending on the method of polymerization, the coating method, the end use, etc., additives selected from the group consisting of initiators, fillers, plasticizers, tackifiers, chain transfer agents, fibrous reinforcing agents, woven and non-woven fabrics, foaming agents, antioxidants, stabilizers, fire retardants, viscosity enhancing agents, coloring agents, and mixtures thereof can be used.

The pressure sensitive adhesive of the present invention includes a microstructured surface on an exposed surface of the adhesive opposite the compliant film. The microstructured surface defines channels in the adhesive. Channels are continuous open pathways or grooves that extend into the adhesive from the exposed surface. The channels either terminate at the peripheral portion of the adhesive layer or communicate with other channels that terminate at a peripheral portion of the article. Upon application of the article onto a substrate, the pathways provide an egress to a periphery of the article for fluid trapped at the interface between the adhesive and the substrate.

The channels are created to define a specific volume per any given area of the microstructured surface of the adhesive. The minimum volume per unit area of the adhesive ensures adequate egress for fluids at the interface of the substrate and the adhesive. Preferably, the channels define a volume of at least  $1 \times 10^3 \mu\text{m}^3$  per any 500  $\mu\text{m}$  diameter circular area in a two-dimensional plane of the adhesive. Most preferably, the channels define a volume in the range of above  $1.0 \times 10^3 \mu\text{m}^3$  to about  $1 \times 10^7 \mu\text{m}^3$  on any 500  $\mu\text{m}$  diameter circular area.

The channels of the present invention at least partially disappear upon final application of the article; in order to provide a desirable adhesion to the exposed surface of the film. The ability of the channels to at least partially disappear is dependent upon the shape of the channel and the rheology of the adhesive. In accordance with the present invention, the channel's size and dimensions are selected for the specific pressure sensitive adhesive compositions to obtain a result of at least 85% according to the percent wet out test discussed in the "Examples" section below. The proper wet out enables a sufficient seal between the article and the substrate.

The shape of the channels can vary widely according to the processing methods, but each preferably has a V-shaped, U-shaped, rectangular or trapezoidal cross section on observation in a transverse direction. FIGS. 2A and 2B show a segmented view of the inventive article 30 highlighting trapezoidal channels 34 in the adhesive 38. The adhesive-backed article 30 includes film 32 and adhesive 38. The trapezoidal channels 34 and corresponding structures 36 are formed in the adhesive 38. Side walls 35 of the structures 36 define side walls for the channels 34.

The limits of dimensions of the channels can be described by use of the aspect ratio. The aspect ratio is defined as the ratio of the greatest microscopic dimension of the channel parallel to the plane of the continuous layer of adhesive to the greatest microscopic dimension of the channel perpendicular to the plane of the continuous layer of adhesive. The aspect ratio is measured by taking the cross-sectional dimensions of the channel at an angle perpendicular to the wall of the channel. Depending on the specific type of channel, the limits of the aspect ratio would be about 0.1 to about 20. For example, the structures of FIG. 7 would define channels that would have a preferred aspect ratio of about 10 to about 15.

Channels are generally created by embossing or forming a plurality of structures into the adhesive. The structures may be present in either a random array or in regular patterns. Individual structures at least partially define a portion of a channel in the adhesive. Selected patterns could include rectilinear patterns, polar

patterns and other conventional regular patterns. A plurality of structures combine to create the continuous channels on the surface of the adhesive.

The shape of the structures formed in the pressure sensitive adhesive to create the microstructured surface can vary. Examples of structure shapes include  
5 but are not limited to those selected from the group consisting of hemispheres, prisms (such as square prisms, rectangular prisms, cylindrical prisms and other similar polygonal features), pyramids, or ellipsoids. Combinations of the different structure shapes can be utilized. The preferred shapes include those selected from the group consisting of hemispheres, prisms, and pyramids. Each individual  
10 structure should typically have a height of greater than about 3 micrometers but less than the total thickness of the adhesive layer, and preferably about 3 micrometers to about 50 micrometers. Additionally, some of the structures may be truncated to provide a surface for additional structures, to control the contact surface of the adhesives, and to improve the wet out of the adhesive. FIG.3A illustrates a  
15 quadrangle pyramid 40 as an illustration of one embodiment suitable for use with the present invention. FIG.3B depicts a truncated quadrangle pyramid 41 that may also be embossed in the pressure sensitive adhesive of the invention.

In the adhesive-backed article of the present invention, the regular patterns or groups of structures have a specific shape and a size to achieve the desired  
20 performance parameters. Therefore, the structures are arranged at a pitch (average value of a distance between similar structural points of adjacent structures) of about 400  $\mu\text{m}$  or less, and preferably about 300  $\mu\text{m}$  or less. A pitch larger than 400  $\mu\text{m}$  may undesirably result in a pattern of the features appearing on the surface of the film after application, thereby causing deterioration in the quality of the article's  
25 appearance.

Double featured structures are an additional embodiment that are suitable for use in the present inventive article. The stacking or use of two structures enhances the positionability of the article by further reducing the initial contacting surface of the adhesive. FIG.4A illustrates a truncated, quadrangle pyramid 42  
30 having an exposed surface 43. A second quadrangle pyramid 44, having a base 45, is positioned on exposed surface 43. FIG. 4B depicts another embodiment

highlighting the double features of the invention. A rectangular feature 46 provides a base 47 for receiving a base 49 of a second smaller rectangular feature 48. In general, the base surface of a second structure is smaller than the exposed surface of the first feature. Additionally, different configurations or shapes may be combined  
5 with base structures to achieve the desirable positioning properties for the present invention.

The positionability of the article is affected by the area of the adhesive that initially contacts the substrate. Preferably, the contact area of the microstructured features results in an initial surface contact area of about 60% or less of the total  
10 area of the adhesive in the plane parallel to the continuous layer of adhesive. The positionability of the present invention is determined by the test noted in the "Examples" section. Preferably, the article of the present invention exhibits a positionability test rating of 2 or better.

FIGS. 5-7 are utilized to demonstrate the various dimensions and  
15 characteristics of the microstructured surface of the pressure sensitive adhesive. The figures represent idealized shapes corresponding to the liner. Those skilled in the art will recognize the pressure sensitive adhesive cannot hold exact tolerances with the scale of the structures utilized in the present invention. Fig. 5 is a segmented perspective view of a pressure sensitive adhesive used in the present  
20 invention. The adhesive 50 has a plurality of structures 52. The pitch  $P$  between the features 52 is not more than 400  $\mu\text{m}$ . The height  $h$  of each feature 52 from the channel 54 is within a range from 3 to 30  $\mu\text{m}$ , the length  $W_1$  of the upside of the channel 54 is within a range from 1  $\mu\text{m}$  to the size of the pitch  $P$  and furthermore a length  $W_2$  of the base of the channel 54 is within a range from 0  $\mu\text{m}$  to the size  
25 enough to make a base angle  $\alpha$  of the feature to a value within a range from 1 to 90°. The aspect ratio of the corresponding channel would be no greater than 20.

FIG. 6 is an illustration of an adhesive 60 having a truncated structure 62 with a second structure 64 positioned on an upper surface 63 of the truncated structure 62. The pitch  $P$  measured from corresponding edges of second structure  
30 64 is not more than 400 $\mu\text{m}$ . The height of each structure from the base of the

channel 66 is in a range of about  $1\mu\text{m}$  to about  $30\mu\text{m}$ . The length  $W_1$  of the upside of the channel 66 is within a range from  $1\mu\text{m}$  to the size of the pitch  $P$  and furthermore a length  $W_2$  of the base of the channel 66 is within a range from  $0\mu\text{m}$  to the size enough to make a base angle  $\alpha_1$  of the structure 62 to a value within a range from  $1$  to  $90^\circ$ . A base angle  $\alpha_2$  of the second structure 64 is within a range from  $1$  to  $90^\circ$ .

Fig. 7 corresponds to the adhesive layer 70 having a microstructured surface 72 in the shape of a quadrangular pyramid. The pitch  $P$  between the structures 72 is equal to the length  $W_1$  of the upside of the channel 74 and is not more than  $400\mu\text{m}$ . The height  $h$  of each structure 72 from the base of the channel 74 is within a range from  $3$  to  $30\mu\text{m}$ . The length  $W_2$  of the base of the channel 74 is  $0\mu\text{m}$ .

The use of a release liner or backing is one method suitable for forming the microstructured adhesive of the present invention. The release liner can be advantageously made of various materials. Preferred materials which the microstructured liner may include, but are not limited to plastics such as polyethylene, polypropylene, polyesters, cellulose acetate, polyvinylchloride, and polyvinylidene fluoride, as well as paper or other substrates coated or laminated with such plastics. These embossable coated papers or thermoplastic films are often siliconized or otherwise treated to impart improved release characteristics. The thickness of the release liner can vary widely according to the desired effect. Furthermore, it is possible to afford structures to the release liner by using various techniques, such as those disclosed in U.S. Patent No. 5,650,215 (Mazurek), herein incorporated by reference in its entirety.

FIG. 8 depicts a liner 80 suitable for creating structures on the surface of an adhesive. The liner 80 includes protrusions 82 that form channels in an adhesive as the adhesive is cast onto the liner.

The article of the present invention is produced by imparting the inventive microstructured surface onto an adhesive with practices conventionally recognized in the art. The features are imparted by embossing the adhesive directly through utilization of molding tools or by coating the adhesive onto a liner or backing

previously embossed with the inventive features. Such methods and practices are fully disclosed in U.S. Patent No. 5,650,215, previously incorporated by reference.

The above-described article can be applied to a variety of substrates, including smooth air-tight surfaces. It is important to match a specific pressure sensitive adhesive to a substrate in order to achieve the desired level of adhesion. Examples of suitable substrates include glass, metal, plastic, wood, and ceramic substrates, and painted surfaces of these substrates. Representative plastic substrates include polyvinyl chloride, ethylene-propylene-diene monomer rubber, polyurethanes, polymethyl methacrylate, engineering thermoplastics (e.g., polyphenylene oxide, polyetheretherketone, polycarbonate), and thermoplastic elastomers. The substrates are generally smooth substrates that accentuate the need for an article with fluid egress. Substrates with rough surface inherently provide an egress for fluids trapped an interface of an applied article because the rough surface permits fluid flow.

The application of the article requires the positioning of the article over the substrate. The microstructured surface of the present invention enable the movement of the adhesive-backed article about the surface of the substrate until pressure is applied to enable adhesive contact and wet out of the adhesive on the surface of the substrate. The appropriate level of pressure and resulting wet out will create a bond between the adhesive and the substrate.

Upon forceful application of the article, the channels permit any entrapped fluid to bleed out around the periphery of the article, thereby eliminating air bubbles. Additionally, the microstructured features of the present invention at least partially collapse during application of the article and thereby increase the amount of adhesive in contact with the substrate. The at least partial disappearance of the channels is indicated through the wet out test, described in the "Examples" below. The present invention demonstrates wet out test results of at least 85%, and preferably at least 95%. The at least partial disappearance of the channels ensures that the article has a desirable level of adhesion to the substrate.

In accordance with the present invention, the microstructured surface of the article is substantially undetectable from the surface of the film and therefore improves the overall appearance of the article. One method for measuring the



appearance involves the use of the surface roughness test procedure, fully described in the "Examples" section. The present invention, upon application of the article onto a substrate, exhibit, from the upper surface of the compliant film, an appearance having no periodicity or repetitive pattern. Additionally, the present invention has a surface roughness no greater than the roughness of the film by itself.

The invention will now be described further by way of the following non-limiting examples.

### EXAMPLES

#### Surface Roughness Test

The surface topography of a film is measured using the RST Plus surface profiling system available from Wyko Corporation in the vertical scanning interferometer mode (VSI) at a magnification of 1.2X and a pixel size of 13.64  $\mu\text{m}$ .

The system uses an interference microscope and a computer algorithm to analyze the surface. In the system, a white light beam passes through a microscope objective to the sample surface. A beam splitter reflects half of the incident beam to a reference surface. The beams from the sample and the reference surface recombine at the beam splitter to form interference fringes which are alternating light and dark bands that are visible when the surface is in focus. The reference arm containing the interferometric objective moves vertically to scan the surface at varying heights using a linearized piezoelectric transducer to control the motion. The interference fringes for white light are present only over a very shallow depth for each focus position so the fringe contrast at a single sample point reaches a peak when the point is in focus. The system starts above the focus point and scans the surface at evenly spaced intervals as the camera captures frames of interference data which contain interference signals for each point on the surface. A computer algorithm processes the data to calculate surface heights.

A single line analysis of the surface, such as those indicated in Figs. 9 and 10, provides a plot of the surface heights along a single line of the sample. The peaks on the plot show whether or not the surface has any periodicity, i.e., a repeating pattern of peaks. The analyses are performed with the tilt term removed

to eliminate extraneous data due to the interferometer configuration. The magnification is 1.2X and the pixel size is 13.64  $\mu\text{m}$ . Evidence of periodicity for an adhesive backed film is generally apparent when the roughness of the adhesive-backed film exhibits a surface roughness greater than the surface roughness of the uncoated film. The surface roughness ( $R_a$ ) is the arithmetic average roughness for the area sampled.

#### Percent Wetout Test

This technique is used to study the wetting of an adhesive having a microstructured surface onto a smooth transparent substrate. The hardware used with this technique consists of a stereo-microscope (Olympus Model SZH-ZB), a video-camera (Cohu Model 4815) mounted on the microscope, a coaxial vertical illuminator (Olympus Model TL2), and a computer (Hewlett-Packard Vectra QS/20) with a video digitizing board (Imaging Technologies PCVISIONplus) installed which allows the computer to capture and digitize an image. Such an image can subsequently be stored and analyzed by commercial software packages (Jandel JAVA). The coaxial vertical illuminator provides light which is sent through the lens (i.e., the optic axis) to illuminate the subject. This light passes through a circular polarizer mounted on the end of the planar objective lens of the microscope. In practice, the procedure is as follows:

1. Apply the adhesive tape onto a glass (or other optically clear and flat) surface with one pass of a 2 kg roller.
2. Position the laminate so that the adhesive/glass interface is viewed through the glass by a stereo microscope.
3. Adjust the sample so that the glass is perpendicular to the optic axis.
4. Adjust the circular polarizer to optimize light intensity and contrast.
5. Using the image analysis software, capture and digitize the image.
6. Set the software grey value window of acceptance to accept only those grey values (i.e., brightness levels) corresponding to the wet areas.

7. Upon application of the tape, analyze the total wetted area as a percentage of the total imaged area.

#### Slide Test for Positionability

- 5 A horizontal glass plate, at about 23°C, was cleaned with methyl ethyl ketone (MEK). A test sample (i.e., pressure sensitive adhesive on the indicated backing), approximately 2.5 cm by 7.5 cm, was draped flat onto the glass plate with the pressure sensitive adhesive side down for approximately 10 seconds. The end edge of the sample was lifted and pulled laterally. The test ratings are as follows:
- 10 1. sample slid freely  
2. sample slid easily with some resistance  
3. sample slid with considerable resistance because of adhesion to the plate, but could be lifted without damage  
4. sample stuck to the plate and could not be repositioned without damage

15

#### Volume of Air Channels

- The volume of the air channels were calculated based on the sizes of the microstructures in a 500 micrometer diameter circle in the liner. The results are reported in cubic microns per 500  $\mu\text{m}$  circle. The volume of air channels is
- 20 calculated and indicated in Table 1.

#### Examples 1 – 11 and Comparative Examples C1-C5

- Embossing rolls were cut with diamond tools or laser machined to provide patterns having varying pitch, depth, widths at the top of the channel and at the base
- 25 of the channel, and base angles. Polyethylene coated paper release liners having a silicone coating over the polyethylenes, such as those available from Rexam or Inncoat, were embossed between a heated rubber roll and each of the embossing roll to produce microstructured liners with ridges. The rubber roll was heated to a temperature of 110°C and the polycoated paper was heated to a surface
- 30 temperature of 110°C before entering the nip between the rubber roll and the embossing roll. The liners traveled around approximately half of the embossing roll,

and then onto a cold can which cooled the liner. The dimensions of the microstructures on the liners are shown in Table 1 and have the shape of inverted square pyramids. The pitch is the distance from one microstructure to the same point on the adjacent microstructure, the height is the height of the microstructure from the base of the channel, W1 is the length of the top of the trapezoidal channel and W2 is the length of the bottom of the trapezoidal channel.

A solvent based acrylic pressure-sensitive adhesive was prepared according to the pressure sensitive adhesive (PSA) copolymer procedure of U.S. Patent No. 4737577, incorporated herein by reference, using 90 parts isooctyl acrylate and 10 parts acrylic acid. The PSA was diluted to about 25% solids with an aziridine crosslinking agent, such as those disclosed in U.S. Patent No. 5,648,425.

The pressure-sensitive adhesive solution was coated onto the microstructured liners to a dried coating thickness of about 30 micrometers. The solution on each liner was dried at 100°C for 10 minutes to form an adhesive film having a microstructured surface defining trapezoidal channels with the approximate dimensions calculated from the liner shown in Table 1.

The exposed adhesive side of each example was then laminated at room temperature to a 50 micron thick primed white plasticized flexible and compliant vinyl (PVC) film primed with an acrylic polymer modified with 2-methylaziridine. The primer was an amine functional acrylic polymer in ethyl acetate. The lamination was made using a two roll nip to provide flat pressure-sensitive adhesive coated PVC films. The films were tested for Appearance, Air Bleed Capability, Slidability, and Wet-out according to the above described Test Methods. Test results are shown in Table 1.

TABLE I

	Pitch $\mu\text{m}$	Height $\mu\text{m}$	W1 $\mu\text{m}$	W2 $\mu\text{m}$	Angle $\alpha$ 1 °	Avg. Vol ( $\mu\text{m}^3$ ) per any 500 $\mu\text{m}$ circular area	Appearance	Air Bleedability	Slidability	Wet-out %
1	126	16	34	17	62	$1.1 \times 10^6$	Good	Good	3	
2	198	21	67	3	39	$1.1 \times 10^6$	Good	Good	3	90.4
3	198	22	28	3	62	$6.1 \times 10^5$	Good	Good	3	93.5
4	197	15	18	1	60	$2.8 \times 10^5$	Good	Good	3	98.4
5	200	15	200	0	9	$1.9 \times 10^6$	Good	Good	2	98.7
6*	197	25	197	3	28	$3.3 \times 10^5$	Good	Good	2	99.0
7	203	20	35	12	60	$8.5 \times 10^5$	Good	Good	3	
8	297	20	35	12	60	$6.0 \times 10^5$	Good	Good	3	
9	198	19	38	22	72	$9.9 \times 10^5$	Good	Good		
10	198	19	28	11	71	$6.3 \times 10^5$	Good	Good		
11	197	20	24	1	60	$4.8 \times 10^5$	Good	Good	3	98.5
C1	1270	22	61	27	52	**	Poor	Good	3	
C2	770	20	143	96	40	**	Poor	Good	3	
C3	508	20	35	12	60	**	Poor	Good	3	
	$\nearrow$									

\*Includes a secondary feature with a base angle of 60°

\*\*Volume indeterminate within a given 500  $\mu\text{m}$  circle

Examples 1-11, produced in accordance with the present invention, exhibit good appearance, good air bleedability, and at least fair slidability. The appearance was determined by visual examination with the unaided eye. A good appearance result indicates no observable underlying structure. A poor appearance results if the pattern is visible. With respect to Examples C1-C3, the average volume per any 500  $\mu\text{m}$  diameter circular area is indeterminate since some 500  $\mu\text{m}$  diameter circular areas do not have channels. Additionally, Examples C1-C3 have poor appearance indicating that patterns created by the channels are visible with the human eye after application.

Samples from each Example measuring approximately 2.54 cm by 2.54 cm were then laminated to a clean glass plate using a plastic squeegee. The samples were then analyzed for surface roughness and periodicity according to the procedure described above. Example C4 is the vinyl film with no adhesive laminated to it, and C5 is the vinyl film with a non-structured PSA laminated to it. Results are shown in Table 2.

TABLE 2

Ex	R <sub>a</sub> Value - $\mu\text{m}$	Single Line Analysis	PSD
1	0.99	Irregular peaks, no periodicity	No spikes
2	0.50	Irregular peaks, no periodicity	No spikes
5	0.85	Irregular peaks, no periodicity	No spikes
6	0.54	Irregular peaks, no periodicity	No spikes
C2	1.60	Definite repeating peaks	
C4	1.31	Irregular peaks, no periodicity	
C5	0.65	Irregular peaks, no periodicity	

Examples 1, 2, 5 and 6 have arithmetic average roughness values comparable to that of a vinyl film (Example C5). Example 2, as illustrated in Fig. 9, shows no periodicity or repeating patterns. Example C2 has a higher arithmetic

average roughness, but more importantly a repeating pattern or periodicity as indicated by the interferometer data. The periodicity of Example C2, as illustrated in Fig. 10, corresponds to the pitch of the channels in the structured surface of the adhesive. The patterns in C2 are detectable with the human eye. Example C4 has a  
5 roughness greater than the vinyl film (Example C5) due to microbubbles present in the adhesive. Examples C4 exhibits no periodicity because the adhesive is not structured.

From the above disclosure of the general principles of the present invention and the preceding detailed description, those skilled in this art will readily  
10 comprehend the various modifications to which the present invention is susceptible. Therefore, the scope of the invention should be limited only by the following claims and equivalents thereof.

What is claimed is:

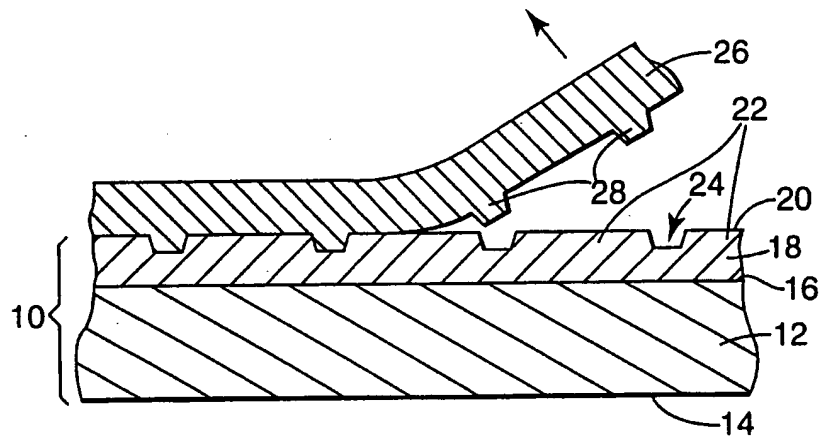
1. An adhesive-backed article, comprising:
  - (a) a compliant film having an upper surface and a lower surface; and
  - 5 (b) a pressure sensitive adhesive bonded to the lower surface of said film, said pressure sensitive adhesive having a microstructured surface, opposite said film, forming channels that define a volume of at least  $1 \times 10^3 \mu\text{m}^3$  per any 500  $\mu\text{m}$  diameter circular area of said adhesive, the channels define exit pathways that provide a fluid egress to a periphery of said article when said article is applied to a
  - 10 substrate, said adhesive-backed article being sealable as indicated by a result of at least 85% according to the percent wet out test, and the channels being substantially undetectable on the upper surface of said compliant film, after final application of said article onto the substrate.
- 15 2. An adhesive-backed article as recited in claim 1, wherein said adhesive-backed article is positionable over a surface of a substrate.
3. An adhesive backed article as recited in claim 2, wherein upon initial contact said article exhibits an initial surface contact area of about 60% or less of the total area
- 20 of said adhesive.
4. An adhesive-backed article as recited in claim 2, wherein said film exhibits a test rating of 2 or better in accordance with the slide test for positionability.
- 25 5. An adhesive-backed article as recited in claim 1, wherein said channels have an aspect ratio in the range of about 0.1 to about 20.
6. An adhesive-backed article as recited in claim 1, wherein the channels have a cross-sectional form of v-grooves, u-grooves, rectangles, trapezoids, or
- 30 combinations thereof.



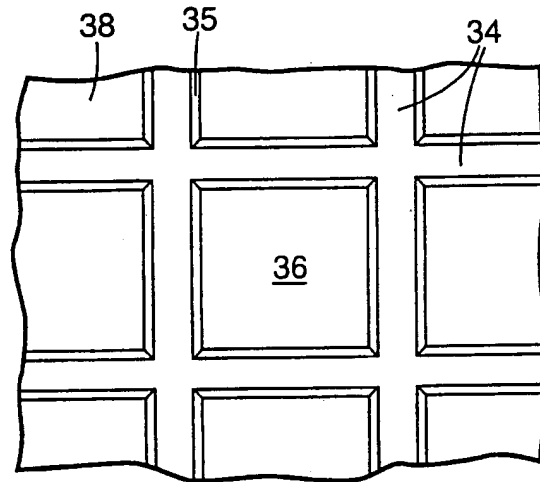
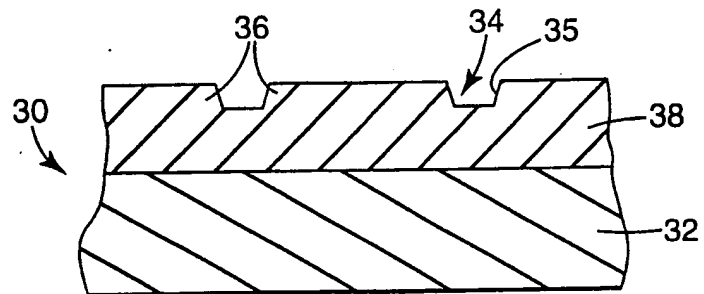
7. An adhesive-backed article as recited in claim 1, wherein said microstructured surface comprises a plurality of structures which at least partially define the channels.
- 5 8. An adhesive-backed article as recited in claim 7, wherein the structures are selected from the group consisting of hemispheres, prisms, pyramids, ellipsoids, or combinations thereof.
9. An adhesive-backed article as recited in claim 7, wherein the structures are  
10 truncated.
10. An adhesive-backed film as recited in claim 9, wherein the truncated structures have a second structure of said adhesive formed thereon.
- 15 11. An adhesive-backed article as recited in claim 7, wherein the structures are randomly placed about the microstructured surface of said adhesive.
12. An adhesive-backed article as recited in claim 7, wherein the structures are  
20 regularly placed about the microstructured surface of said adhesive.
13. An adhesive-backed article as recited in claim 12, wherein the structures are positioned at a pitch in the range of about 400  $\mu\text{m}$  or less.
14. An adhesive-backed article as recited in claim 1, wherein said article, upon  
25 application of said pressure sensitive adhesive onto a surface of a substrate, exhibits from the upper surface of said compliant film an appearance having no periodicity and no surface roughness beyond the surface roughness of the film by itself in accordance with the surface roughness test procedure.
- 30 15. An adhesive-backed article as recited in claim 1, further comprising a primer layer bonding said film to said pressure sensitive adhesive.

16. An adhesive-backed article as recited in claim 1, further comprising a release liner bonded to the microstructured surface of said pressure sensitive adhesive.
- 5 17. An adhesive-backed article as recited in claim 1, wherein said adhesive-backed article is applied onto a substrate.
18. An adhesive-backed article, comprising:
- (a) a compliant film having an upper surface and a lower surface;
- 10 (b) a pressure sensitive adhesive having a first surface and second surface, said first surface bonded to the lower surface of said film; and
- (c) a release liner bonded to the second surface of said pressure sensitive adhesive, said release liner having a microstructured surface that defines a microstructured surface in the second surface of said pressure sensitive adhesive, the
- 15 microstructured surface in said adhesive forming channels that define a volume of at least  $1 \times 10^3 \mu\text{m}^3$  per any 500  $\mu\text{m}$  diameter circular area of said adhesive, the channels define exit pathways that provide a fluid egress to a periphery of said article when said release liner is removed and said article is applied to a substrate, said adhesive-backed article being sealable as indicated by a result of
- 20 at least 85% according to the percent wet out test, and the channels being substantially undetectable on the upper surface of said compliant film, after removal of the release liner and final application of said article onto the substrate.

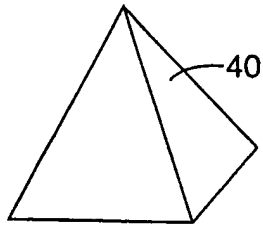
1/6

**Fig. 1**

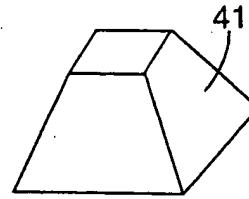
2/6

**Fig. 2A****Fig. 2B**

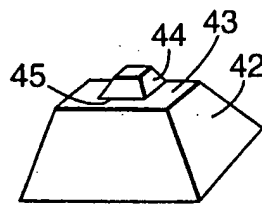
3/6



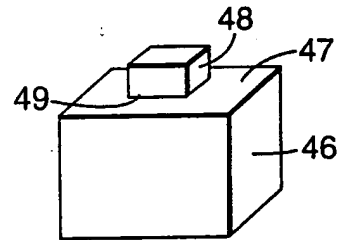
**Fig. 3A**



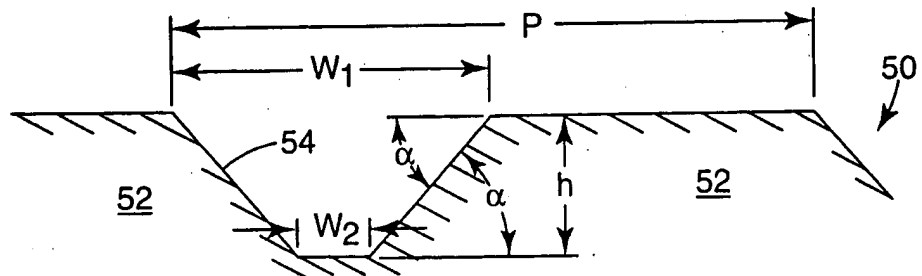
**Fig. 3B**



**Fig. 4A**

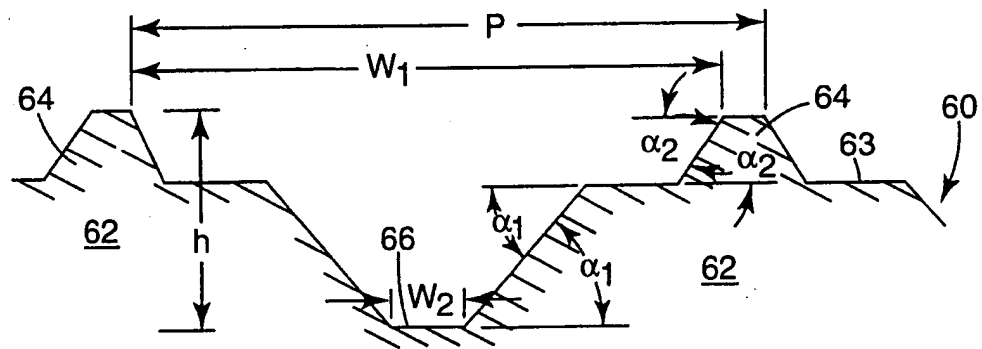
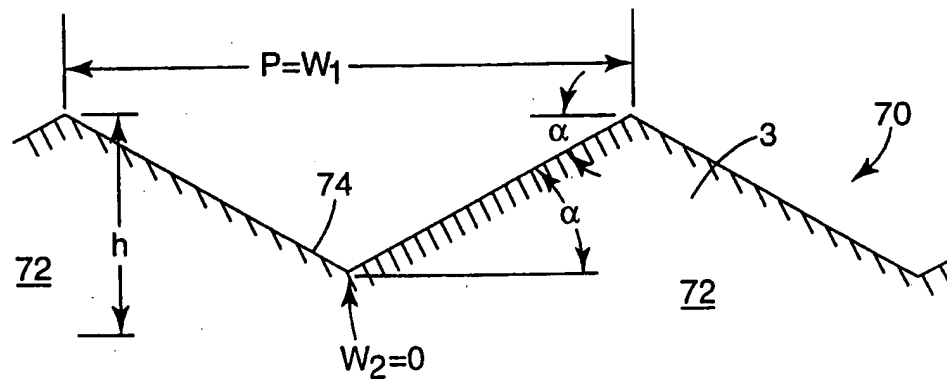


**Fig. 4B**

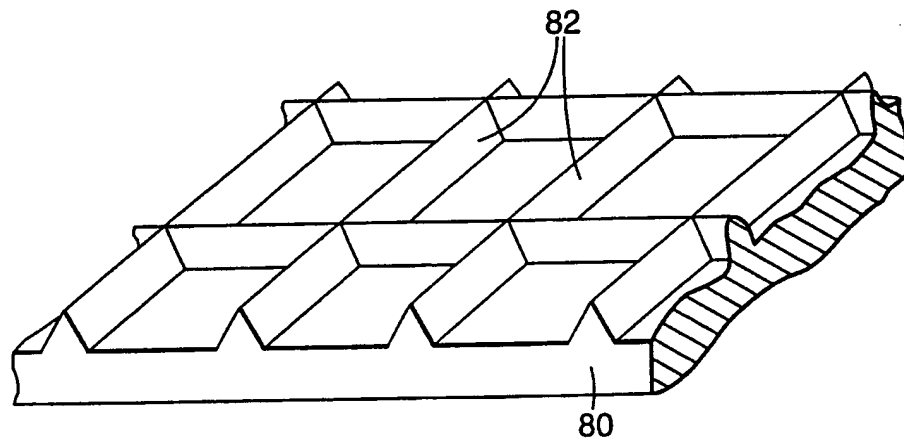


**Fig. 5**

4/6

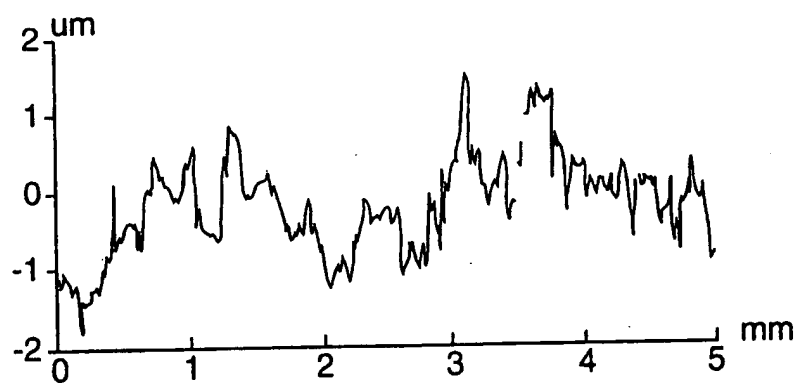
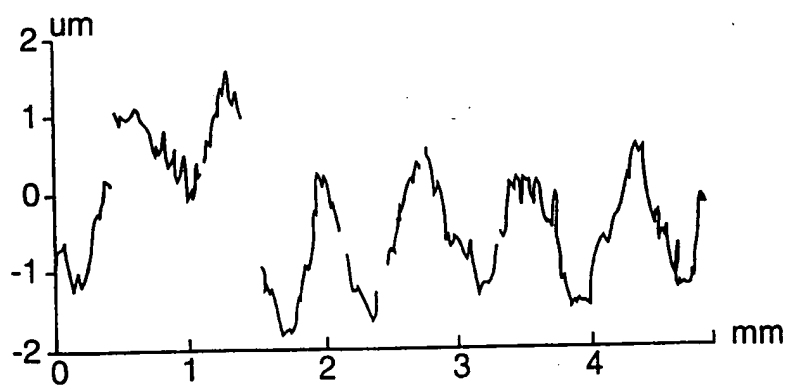
**Fig. 6****Fig. 7**

5/6



**Fig. 8**

6/6

**Fig. 9****Fig. 10**



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 99/23020

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C09J7/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 00525 A (MINNESOTA MINING & MFG) 6 January 1994 (1994-01-06) page 3, line 22 -page 2, line 2 page 7, line 22 -page 8, line 3 figure 1 page 18, line 27 -page 19, line 26 example 36 table 6	1-4, 6-9, 12, 14-18
X	WO 98 29516 A (MINNESOTA MINING & MFG) 9 July 1998 (1998-07-09) abstract page 11, line 20 - line 27 page 14, line 6 examples 1-3 table 1	1, 6-18

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "S" document member of the same patent family

Date of the actual completion of the international search

20 January 2000

Date of mailing of the international search report

01/02/2000

Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Schlicke, B

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/23020

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 650 215 A (MAZUREK MIECZYSLAW H ET AL) 22 July 1997 (1997-07-22) cited in the application column 3, line 21 - line 50 column 11, line 48 - column 12, line 54 column 17, line 18 - line 36 examples 18-22 table 3 ---	1-18
P,X	WO 99 35201 A (ABE HIDETOSHI ;MINNESOTA MINING & MFG (US)) 15 July 1999 (1999-07-15) abstract example 1 page 6, line 18,19 ---	1-3,6-8, 12,14, 16,17
X	EP 0 279 579 A (BRIDGESTONE CORP) 24 August 1988 (1988-08-24)  page 2, line 21 - line 26 page 3, line 6 - line 22 page 4, line 19 - line 24 figures 1-3 ---	1,6,7,9, 12,14, 16-18
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 10, 31 October 1997 (1997-10-31) & JP 09 141812 A (OJI PAPER CO LTD), 3 June 1997 (1997-06-03) abstract -----	1,14, 16-18

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/23020

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9400525 A	06-01-1994	AU 4630493 A	24-01-1994
		BR 9306618 A	08-12-1998
		CN 1086837 A	18-05-1994
		DE 69317890 D	14-05-1998
		DE 69317890 T	03-09-1998
		EP 0647256 A	12-04-1995
		ES 2114612 T	01-06-1998
		JP 7508303 T	14-09-1995
		MX 9303746 A	31-01-1994
		US 5362516 A	08-11-1994
		US 5296277 A	22-03-1994
WO 9829516 A	09-07-1998	AU 3290897 A	31-07-1998
		EP 0951518 A	27-10-1999
US 5650215 A	22-07-1997	CA 2173855 A	04-05-1995
		DE 69422057 D	13-01-2000
		EP 0725809 A	14-08-1996
		JP 9504325 T	28-04-1997
		WO 9511945 A	04-05-1995
WO 9935201 A	15-07-1999	JP 11209704 A	03-08-1999
		AU 2023699 A	26-07-1999
EP 0279579 A	24-08-1988	JP 63193982 A	11-08-1988
		JP 63223081 A	16-09-1988
		DE 3880341 A	27-05-1993
JP 09141812 A	03-06-1997	NONE	